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A mathematical model for an isothermal direct ethanol fuel cell

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Abstract. In this work we have developed a three-dimensional mathematical model to analyze a direct ethanol fuel cell. The numerical simulation of reactive flow was done based on the central finite difference method. The equations were integrated in time using the simplified Runge-Kutta multistage scheme. Obtained results are in agreement with experimental data found in the literature for various feed concentrations of ethanol and different cell operation temperatures. In this way, this work contributes with the development of a model for direct ethanol fuel cells taking into account all losses overpotentials at anode and cathode, providing a better understanding of the chemical energy conversion in electricity, and its numerical simulation.

Keywords. Fuel Cells, Ethanol, Proton Exchange Membrane.

1 Introduction

The fuel cell is an electrochemical device that converts chemical energy directly in electricity. Fuel cell systems with high energy density are potential candidates to supply the forthcoming energy demand. The energy density of fuel cells for mobile devices is growing 3 to 10 times more than the energy density of lithium batteries currently in use [?]. In this work, a PEMFC is fed with ethanol fuel. The importance and advantages of ethanol as fuel are already recognized worldwide. Ethanol has been chosen as fuel by several factors, such as: it has higher energy density, is less toxic than methanol, can be produced from renewable sources containing sugar [?], has lower crossover rate and affects less severely the performance of the cathode than the methanol [?, ?].

Mathematical models are needed to optimize the design of fuel cells for the development of power systems. To understand and improve the performance of PEMFC systems, several mathematical models have been proposed to estimate its voltage and current [?]. However, most studies consider the flow in fuel cell using one-dimensional models [?, ?, ?]. In a recent paper, Abdullah et al. [?] made a review of direct ethanol fuel cell and reported that they found only one work focused on three-dimensional models. Therefore, among the major
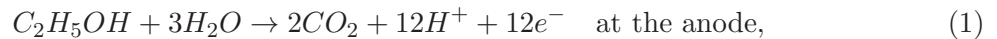
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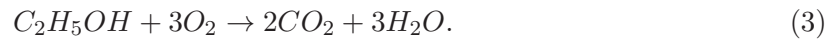[2]dbortoli@mat.ufrgs.br

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advances in the development and improvement of DEFC cited by Abdullah et al. [**?**], are the urgent need to develop a multi-phase and a multi-dimensional mathematical model that can capture the complex physical and chemical behavior in real DEFC systems. Thus, this paper proposes a three-dimensional model for calculating the flow inside of the DEFC considering all the losses on potential.

2   Proton Exchange Membrane Fuel Cell

A catalyst $(PtRu/C)$ is used to break the fuel molecules at the anode. The electro-chemical reactions that take place inside the cell are given by:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- \quad \text{at the anode,} \tag{1}$$

$$3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O \qquad \text{at the cathode,} \tag{2}$$

corresponding to the overall reaction

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O. \tag{3}$$

In the Figure 1 is shown the schematic diagram of PEMFC modeled in this work. The mixture of ethanol and water is inserted into the anode side, which reacts to form carbon dioxide, protons and electrons. The protons pass preferably to the cathode through the membrane and the electrons through an external circuit. On the cathode side, the air reacts with the protons and electrons formed at the anode to produce water vapor [**?**].
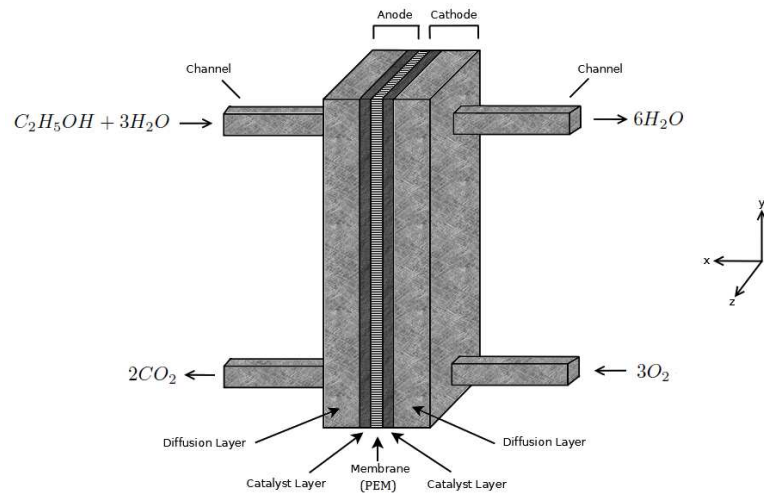

Figure 1: Schematic diagram of three-dimensional PEMFC

3   Governing Equations

For both anode and cathode, the equations for the flow and the concentration of species have the same form. The equations for the flow are the continuity, momentum and species

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conservation.

Continuity equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0. \tag{4}$$

Momentum equation:

$$\frac{\partial}{\partial t}(\rho u) + \rho u \cdot \nabla u = -\nabla p + \mu \nabla^2 u + \rho S_u, \tag{5}$$

where ρ is the density, u_i is the velocity component in the direction i, with $i = 1, 2, 3$, μ is the viscosity and p is the pressure. Table 1 shows the source term S_u, where ε_d and ε_c are the porosities of the diffusion layer and of the catalyst layer, respectively, and k is the permeability of the water (k_{H_2O}) in the anode and the permeability of air (k_{O_2}) in the cathode. The fluid velocity in the diffusion and catalyst layers is described by Darcy's law and in the membrane it is assumed velocity equal to zero due to the negligible convective velocity through the membrane [**?**].

Table 1: Source term S_u.

	Channel	Diffusion layer	Catalyst layer
S_u	0	$-\varepsilon_{cd}\frac{\mu}{k}u$	$-\varepsilon_{cc}\frac{\mu}{k}u$

Species equations:

Each species satisfies a equation of type

$$\frac{\partial Y_k}{\partial t} + \rho u \cdot \nabla Y_k = \rho D_k^{\text{eff}} \nabla^2 Y_k + S_k, \qquad \text{with} \quad \sum_k Y_k = 1. \tag{6}$$

where Y_k is the mole fraction of species k, S_k is the mass generation rate for species k per unit volume, and D_k^{eff} is the effective diffusion coefficient of the kth component. The Table 2 presents the term S_k, where j_a is the volumetric current density in the anode, j_c is the volumetric current density in the cathode, and M_{Et}, M_{H_2O}, M_{CO_2} and M_{O_2} are the molecular weights of ethanol, water, carbon dioxide and oxygen, respectively. The source term, S_k, is zero inside of the channels and in the diffusion layer.

Table 2: Source term S_k in the catalyst layer.

Anode			Cathode	
ethanol	water	carbon dioxide	oxygen	water
$-\frac{M_{Et}}{12F}(j_a + j_{xover})$	$-\frac{M_{H_2O}}{4F}j_a$	$\frac{M_{CO_2}}{6F}j_a$	$-\frac{M_{O_2}}{4F}(j_c + j_{xover})$	$\frac{M_{H_2O}}{2F}(j_c + j_{xover})$

The ethanol crossover through the membrane is caused by diffusion and electro-osmotic drag, and the flux can be obtained from

$$j_{xover} = \frac{\lambda_{Et}I}{F} + \varepsilon_m^{1.5} D_m^{Et} \frac{dC_{Et}^m}{dz}, \tag{7}$$

where C_{Et}^m is the ethanol concentration in the membrane, λ_{Et} the electro-osmotic drag coefficient of ethanol, I is the average current density of the cell e D_m^{Et} is the diffusion coefficient of ethanol in the membrane.

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4   Cell voltage

One of the reasons why is important to model fuel cells is to determine why the effective voltage differs from the thermodynamically predicted theoretical voltage. In this case, the overall cell voltage can be obtained using the following relationship

$$V_{cell} = E^0_{cell} - (\eta_{ativ} + \eta_{ohm} + \eta_{con}), \tag{8}$$

where η_{ativ} is the loss due to activation, η_{ohm} are the losses due to ohmic resistance, η_{con} are the losses due to concentration, V_{cell} is the cell potential and E^0_{cell} is the reversible potential of DEFC, given by

$$E^0_{cell} = \frac{-\Delta G^0}{nF}. \tag{9}$$

The modified Butler-Volmer equation is used to determine the transfer of current densities at the anode (j_a) and at the cathode (j_c) [?]:

$$j_a = j_0 \frac{C_{0,Et}}{C_{F,Et}} \exp\left(\frac{\alpha_a nF \eta_{con,a}}{RT}\right), \tag{10}$$

$$j_c + j_{xover} = j_0 \frac{C_{O,c}}{C_{O,wv}} \exp\left(\frac{\alpha_c nF \eta_{con,c}}{RT}\right), \tag{11}$$

where j_0 is the exchange current density (at the anode and cathode), $C_{0,Et}$ is the ethanol concentration in the catalyst layer, $C_{F,Et}$ is the ethanol feed concentration, $C_{O,c}$ is the concentration of oxygen in the catalyst layer, $C_{O,wv}$ is the concentration of oxygen in water vapor, α_a is the anode transfer coefficient, α_c is the cathode transfer coefficient, n is the number of electrons transferred, F is the Faraday constant, R is the universal gas constant, T is the temperature, $\eta_{a,con}$ and $\eta_{c,con}$ is the concentration overpotential at the anode and cathode.

Activation overpotential:

The relation between activation overpotential and current density is [?]

$$\eta_{a,act} = \frac{RT}{\alpha_a nF} \ln\left[\frac{j_a}{(C_{Et}C_{H_2O})^{1/4}}\right], \tag{12}$$

where C_{Et} is the local ethanol concentration and C_{H_2O} is the local water concentration.

Ohmic losses:

The ohmic losses can be written as

$$\eta_{ohm} = j_a \times \left[\frac{t_m}{(0.005139\theta - 0.00326)\exp[1268(1/303 - 1/T)]} + R_b\right], \tag{13}$$

where θ is the Nafion® membrane hydration parameter, t_m is the thickness of the membrane and R_b is the collective area specific resistance.

Concentration overpotentials:

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The model equation for anode and cathode concentration overpotential is given respectively by

$$\eta_{con,a} = \frac{RT}{\alpha_a nF} \ln\left(\frac{j_{lim,a}}{j_{lim,a} - j_a}\right), \tag{14}$$

$$\eta_{con,c} = \frac{RT}{\alpha_c nF} \ln\left(\frac{j_{lim,c}}{j_{lim,c} - (j_c + j_{xover}^{pdc})}\right) \tag{15}$$

where $j_{lim,a}$ and $j_{lim,c}$ are the limiting current at the anode and cathode.

5   Numerical Results

A code in fortran90 was developed for the solution of the equations (4), (5) and (6). The finite difference method was used for the discretization of the derivatives and the Runge-Kutta simplified method was used for the time integration. The mesh used to obtain the numerical results contains $50 \times 100 \times 100$ cells. The Figure 2 refers to a cut in the middle of the fuel cell and shows the contour lines of velocity, for ethanol flow rate of 1.0 ml min^{-1} and pressure of $p = 1$ bar at the anode.
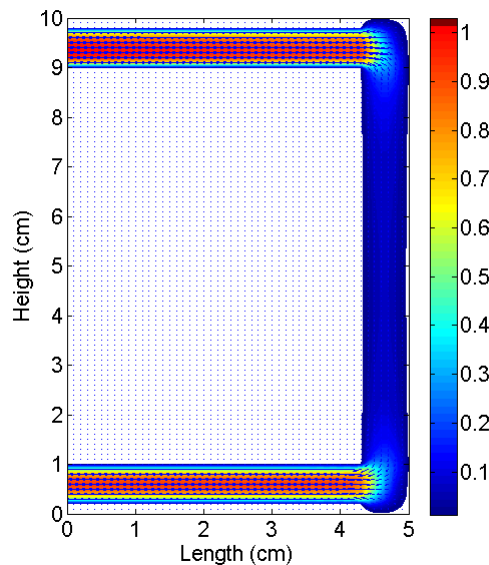

Figure 2: Velocity contour lines inside the cell (anode side)

The Figure 3 shows the current density versus cell voltage for different feed concentrations of ethanol at 315K in the anode. The symbols represent the experimental data [?] and the lines represent the results obtained with the model. The Figure 3 shows that the cell voltage increases with the increase of ethanol concentration for a given value of current density. Obtained results are in good agreement with experimental data given by Pramanik and Basu [?].
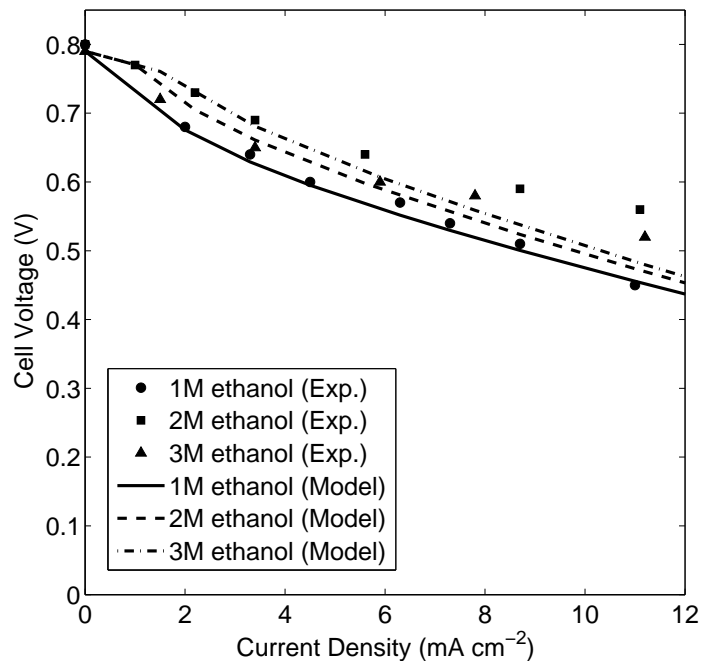
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Figure 3: Current density vs. cell voltage for different concentrations of ethanol of a PEMFC.

6   Conclusions

In this work, it was developed a three-dimensional model for a direct ethanol PEM fuel cell. The reactive flow was solved based on the Navier-Stokes equations for the flow, and the mass fraction equations of each species, considering losses overpotentials for anode and cathode sides. Obtained results are in agreement with experimental data found in the literature for different concentrations of ethanol. The flow inside the channels is parabolic and the velocity decreases near the membrane due to mass conservation, where cavity area increases. As most of the work found in the literature is focused on one-dimensional fuel cell models, this paper contributes with the development of a three-dimensional mathematical model for direct ethanol PEM fuel cells considering all losses (activation, ohmic and concentration).

7   Acknowledgements

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